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Production and destruction of CF_x radicals in radio-frequency fluorocarbon plasmas

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Spacially resolved densities of CF , CF_2 , and CF_3 radicals in capacitively coupled 13.56 MHz radio-frequency (rf) discharges in CF_4 and CHF_3 were determined by means of infrared absorption spectroscopy employing a tunable diode laser spectrometer. It was established that the stationary CF_2 density and density profile in a CF_4 plasma depend strongly on the electrode material. This is attributed to different sticking coefficients of CF_2 on different surfaces. Furthermore, it was found that the densities of all CF_x radicals increase near the electrodes at high gas pressures and rf powers in a CHF_3 plasma. This leads to the conclusion that production of CF_x radicals takes place in the sheath region close to the electrodes. It is proposed that collisions between ions and source gas molecules are responsible for this production of CF_x radicals. In the presence of a destruction process in the plasma glow (e.g., by three-body recombination with other radicals) and the absence of a fast surface loss process this results in the observed increase of CF_x densities near the electrodes. In order to study the radical kinetics time dependent measurements were performed during power modulation of the plasma. It was found that the decay time of the CF_2 density in the afterglow of a CF_4 plasma is much shorter than the corresponding decay time in a CHF_3 discharge. This suggests that the surface loss is relatively less important in the latter case, in agreement with measurements of spatial density distributions. This is explained by the presence of a $(CF_x)_n$ layer, which is readily deposited on the electrodes in a CHF_3 discharge, and by low sticking probabilities of CF and CF_2 radicals on such a layer. © 1996 American Vacuum Society.

I. INTRODUCTION

Capacitively coupled radio-frequency (rf) plasmas are widely used in the semiconductor industry fabricating small structures in semiconductor substrates using dry etch processes. Despite the fact that capacitively coupled rf plasmas find many applications, the detailed mechanisms that are responsible for the production and destruction of the species present in the plasma are not yet totally clear. The influence of plasma-wall interactions on the densities and kinetics of neutral radicals present in the plasma especially is still not well understood. In the last few years active spectroscopic techniques have been applied, like laser induced fluorescence (LIF)¹⁻⁴ and infrared absorption spectroscopy,⁵⁻⁹ that can yield quantitative data on densities of species with good spatial and time resolution. Measurements employing these diagnostics show that in capacitively coupled rf plasmas in some fluorocarbon gases a large part of the source gas may be converted into other stable fluorocarbon species and/or etching reaction products and that radical densities reach typically a few percent of the total gas density.⁸

Booth *et al.*¹ used LIF to measure the spatial distribution of CF_2 in a CF_4 plasma with Al electrodes at several pressures. At 50 mTorr pressure and 0.4 W/cm² rf power density they found that the profile is more or less flat, except for a small region near the rf powered electrode where the density decreases towards the electrode. At 500 mTorr and 0.9 W/

cm² rf power density they found that the CF_2 density increases significantly close to the rf electrode. At the same pressure, but applying 0.4 W/cm² rf power density, this increase disappears almost completely. These results were confirmed by measurements of Hansen *et al.*,³ who studied the spatial distribution of CF_2 using LIF in a 300 mTorr $CF_4/O_2/Ar$ (87.5/10.4/2.1) plasma with electrodes made of Al, Cu, and SiO_2 . With Al and SiO_2 electrodes the effect was comparable to the one found by Booth *et al.*¹ With copper electrodes the overall CF_2 density is significantly lower than with the other studied materials. Moreover, in this situation the CF_2 density is about 50% lower at the electrodes than in the plasma, indicating that enhanced surface loss of CF_2 occurs when copper electrodes are used. Hansen *et al.* proposed that catalytic destruction of CF_2 occurs on copper electrodes.³

A similar increase in the CF_2 density near the electrodes at higher gas pressures was observed^{5,8} by the authors of this article using tunable diode laser infrared absorption spectroscopy in capacitively coupled rf plasmas in CHF_3 , C_2F_6 , and CF_2Cl_2 . In previous works CF_2 production by chemical sputtering of a layer that is continuously deposited by other radicals was suggested as a possible mechanism in explaining the observed density increase near the electrodes. In order to test the validity of this hypothesis and establish which radical is responsible for the deposition, it is necessary to determine the spatial profile of all three CF_x ($x=1,2,3$) radicals and to check whether any of these radicals shows a clear drop in density towards the electrode in the situation where an increase in the CF_2 density is observed. In this article measure-

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ments of CF , CF_2 , and CF_3 will be presented as a function of the axial position in both CHF_3 and CF_4 plasmas. Moreover, the kinetics of all three radicals after plasma extinction and initiation are studied to obtain more information on the production and loss processes, which result in the observed spatial distributions of the radical densities.

II. EXPERIMENT

The experimental setup and the measurement procedure have been explained extensively in an earlier article,⁵ so only a brief description will be given here. The experiments were performed in a 13.56 MHz capacitively coupled rf plasma with a 12.4-cm-diam planar parallel-plate configuration and 3 cm electrode separation. The plasma generator can be controlled directly from the measurement computer to allow for time-resolved measurements after plasma initiation or extinction. The infrared beam of a Laser Photonics tunable diode laser system (TDLS) enters and exits the reactor through two BaF_2 windows. The beam is aligned parallel to the electrodes and a system of lenses reduces the beam diameter and focuses it in the center of the reactor to obtain a spatial resolution of about 1 mm. After passing the reactor the radiation is focused onto a photovoltaic mercury cadmium telluride (MCT) detector. The wavelength of the laser beam is modulated by modulating the current through the laser diode, allowing for phase-sensitive detection by a lock-in amplifier. Absorption spectra are obtained by varying the dc laser current. Good time resolution can be obtained when a high modulation frequency is used and the time constant of the lock-in amplifier is kept small. In our case values of 30 kHz and 1–10 ms are used, respectively. To correct for any changes in window transmission, partial blocking of the laser beam close to the electrodes, and laser intensity drift, the absolute laser intensity is measured after each spectrum. This is done by switching off the laser for a short time and measuring the transient signal using an A/D converter. This yields the total intensity which is subsequently used to scale the measured absorption spectrum. In the axial scans, when the beam is situated less than 1.5 mm from the electrodes, some laser intensity fluctuation is observed, probably due to reflections on the surface itself. These measurement points have therefore been discarded. Measurements in the afterglow and in the initiation phase of the plasma were performed by a computer-controlled automatic procedure in which first a small part of the spectrum is determined with the plasma on. Within this spectrum the center of the absorption peak of interest is determined and the laser current is set to the corresponding value. Then the plasma is switched off for some time (typically 0.5–1 s) and reignited again. This procedure is repeated several times and the results are block averaged to improve the signal-to-noise ratio.

III. IDENTIFICATION OF THE SPECTRA OF CF , CF_2 , AND CF_3

Identification of absorption lines of CF_x radicals in fluorocarbon rf plasmas is a difficult task because of the overlap

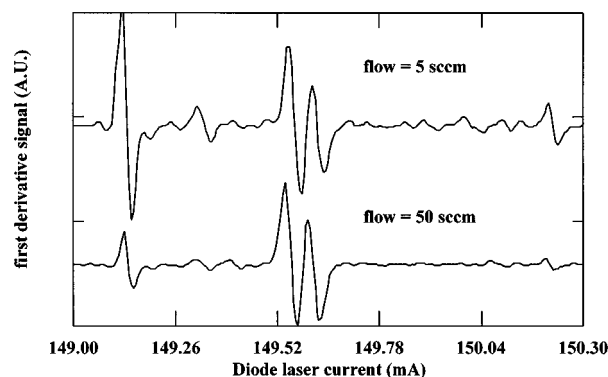


FIG. 1. Absorption spectrum of the vibration-rotation transition of the CF fundamental band around 1298.42 cm^{-1} in a 300 mTorr CHF_3 plasma for two values of the flow rate. The ${}^2\Pi_{1/2}R(3.5)$ transition is split into two components due to Λ -type doubling. It is clear that CF is not removed by gas flow.

of the radical absorption spectra with those of stable molecules like CF_4 and C_2F_6 . We use the fact that stable molecules are removed by the gas flow,¹⁰ while the radical densities are flow independent. Thus, by comparing the spectra for different gas flow rates the radical absorption lines can be found. CF is a diatomic molecule, so it shows only one absorption band, with its origin located¹¹ at 1286.1281 cm^{-1} . This is very close to the band origin of the CF_4 ν_3 band, located^{12,13} at 1283.2 cm^{-1} . Therefore most of the strongest CF transitions are found in a region where strong CF_4 lines are also present. However, we found two lines at 1298.284 and 1298.429 cm^{-1} that we attribute to the ${}^2\Pi_{3/2}R(3.5)$ and ${}^2\Pi_{1/2}R(3.5)$ transitions of CF, respectively, and which are not close to any CF_4 lines. In Fig. 1 the first derivative spectrum of the ${}^2\Pi_{1/2}R(3.5)$ transition (split into two components as a result of Λ -type doubling) in a CHF_3 plasma is shown at two flow settings. It is easy to distinguish the absorption lines of CF, which are independent of flow from the CF_4 lines which disappear at high flow rates.

In the detection of CF_3 similar problems are encountered. The CF_3 ν_3 band with its origin located¹⁴ at 1260.1619 cm^{-1} overlaps strongly¹³ with both the ν_3 bands of ${}^{12}\text{CF}_4$ and ${}^{13}\text{CF}_4$ as well as the ν_7 band of C_2F_6 located around 1250 cm^{-1} . However, around $\sigma=1269.05\text{ cm}^{-1}$ we have found a CF_3 peak in the first derivative spectrum that is free from any significant background of CF_4 or C_2F_6 . From a simulation of the CF_3 ν_3 spectrum in this region based on its rotational constants¹⁴ it was found that this peak in the first-derivative spectrum consists of a superposition of a few strong lines in the CF_3 spectrum. In Fig. 2 the first derivative signal in a 100 mTorr CHF_3 plasma is shown again for two values of the flow rate. As in case of the CF spectrum, it is easy to single out the CF_3 lines, because CF_3 is also not lost by gas flow. However, as it is a superposition of several lines, the absolute CF_3 density cannot be easily obtained.

Compared to CF and CF_3 , the measurement of CF_2 absorption is relatively easy. Although there is some minor overlap between the CF_2 ν_3 band ($\sigma_0=1114.4435\text{ cm}^{-1}$) and the C_2F_6 ν_5 band around 1115 cm^{-1} , there are several

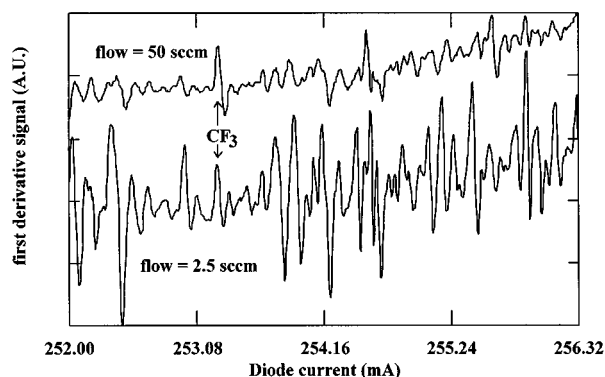


FIG. 2. Absorption spectrum of the ν_3 transition of the CF_3 radical around 1269.1 cm^{-1} in a 100 mTorr CHF_3 plasma for two values of the flow rate. Although there is a large contribution of CF_4 transitions, one CF_3 transition that is free from overlap with CF_4 can be identified. It can be seen also that CF_3 is not lost by gas flow.

lines of CF_2 available around 1096 cm^{-1} which show no overlap with the lines of any other species.⁵

IV. RESULTS AND DISCUSSION

A. Spatial profiles of CF , CF_2 , and CF_3 in CHF_3

In Fig. 3 the relative CF_2 densities as a function of the axial position in a CHF_3 plasma at 300 mTorr are shown for two values of the rf power (0.83 and 0.083 W/cm^2). The axial profiles were scaled using the density values at 15 mm. It can be seen that at high rf power density the CF_2 density increases considerably near the electrodes but is relatively constant over the glow region of the plasma. To make sure that this effect does not result from possible temperature gradients in the plasma, the temperature of CF_2 (obtained from the linewidth) was determined as a function of the axial position.¹⁵ It was established that the temperature in both CHF_3 and CF_4 plasmas is, at most, several degrees above room temperature and does not depend on the axial position. At low rf power density the increase of the CF_2 density near

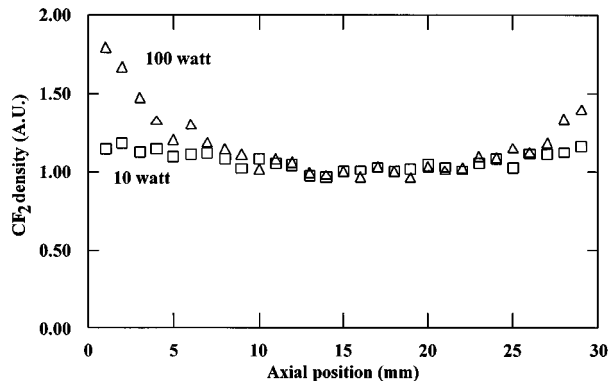


FIG. 3. Spatial profile in the axial direction of the CF_2 density in a 300 mTorr CHF_3 plasma for two values of the rf power. The rf powered electrode and the grounded electrode are situated at $z=0$ and $z=30$ mm, respectively. The values were scaled using the densities at $z=15$ mm. The density increase near both electrodes disappears at low values of the rf power.

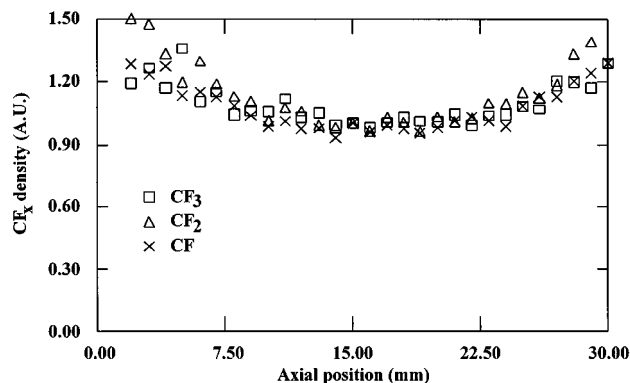


FIG. 4. Measurement of the axial profile of the CF , CF_2 , and CF_3 density in a 300 mTorr CHF_3 plasma at 100 W rf power. The densities have been scaled using their values at $z=15$ mm.

the electrodes disappears completely, in agreement with the LIF measurements of Booth *et al.*¹ who found a similar behavior in CF_4 plasmas.

To investigate the production mechanism of CF_2 near the electrodes also the axial profiles of CF and CF_3 have been determined. Figure 4 shows the axial profiles of CF , CF_2 , and CF_3 for a 300 mTorr, 0.83 W/m^2 CHF_3 plasma. It is clear that for these conditions a significant increase in density for all radicals is observed at both electrodes.

From the dependencies of the three CF_x radicals it appears that surface production of CF_x radicals takes place. The fact that the same behavior is observed for all three radicals means that the previously suggested mechanism,⁵ according to which the production of CF_2 near the electrodes is caused by chemical sputtering of a $(\text{CF}_x)_n$ layer that is continuously deposited on the electrodes by other radicals, cannot explain the observed profiles. Alternatively, in the same article it was suggested that ion-molecule reactions in the sheath could produce radicals in the sheath regions close to the electrodes. A possible problem with this mechanism is that the fluxes of CF_x , produced in the sheath region of a CHF_3 plasma (which can be calculated from the observed CF_x gradients and the diffusion coefficient) are more than an order of magnitude higher than the ion fluxes that can be calculated from the ion densities at the sheath edge and the Bohm velocity:

$$\text{neutral flux: } \Phi_{\text{rad}} = D_{\text{rad}} \partial n_{\text{rad}} / \partial x \approx 3 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}, \quad (1)$$

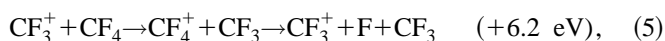
$$\text{ion flux: } \Phi_{\text{ion}} = n_{\text{ion}} v_{\text{Bohm}} \approx 3 \times 10^{19} \text{ m}^{-2} \text{ s}^{-1}. \quad (2)$$

Here the diffusion coefficient of CF_2 in CF_4 , determined by Arai *et al.*¹⁶ $D_{\text{rad}} = 0.02 \text{ m}^2 \text{ s}^{-1}$ was substituted and the CF_2 density gradient has been determined from Fig. 4. The ion density was measured by Haverlag:¹³ $n_+ = 10^{17} \text{ m}^{-3}$ and the Bohm velocity v_{Bohm} in an electronegative plasma is about 300 m/s.¹⁷

Equations (1) and (2) show that radical production by recombining positive ions at the surface cannot account for the observed phenomena. On the other hand, the positive ions are the only active species in the sheath that can produce large amounts of radicals. Therefore in a CHF_3 plasma at

pressures around 300 mTorr we have to assume that each ion that enters the sheath produces at least ten radicals there in order to explain the observed radicals fluxes.

The fact that inelastic ion–molecule collisions do indeed occur in the sheath has been shown by Snijkers,¹⁸ who measured the energy spectra of several ions arriving at the rf and grounded electrodes of a CF₄ plasma. Since in the ion energy spectra at higher pressures (>50 mTorr) the primary saddle structures are completely absent and most of the ions reach the electrodes with low energies, it can be concluded that the ions must have undergone several inelastic collisions before arriving at the electrodes. To illustrate how these collisions could result in radical production, the following set of reactions (along with the energy differences between the situations after and before the reactions) is given as an example of possible sheath radical production in a CF₄ plasma:



Here reactions (3) and (4) would produce CF₂, reaction (5) would produce CF₃, and reactions (3), (6), and (7) would produce CF. Of course there are many other reactions possible that could end up in the production of radicals. Since at the end of these sets of reactions the original ion is again obtained, the reaction chain could in principle be repeated several times, thus producing several radicals per incoming ion. Similar reactions can occur in a CHF₃ plasma. From reactions (3)–(7) it can be seen that the energy needed to produce CF₂ or CF₃ is 6–8 eV. Since the ions in principle can gain a potential energy given by the sheath voltage (>100 V), this means that each ion can yield up to 20–30 radicals, which is more than enough to explain the increased radical production in the sheath and consequently the observed density profiles. The fact that the increase of the radical density near the electrodes almost disappears at low rf power (see Fig. 3) can then be explained by the fact that the sheath voltage decreases with decreasing power and therefore less radicals are produced per ion at low power levels.

A problem with the proposed mechanism is that there are no cross sections available for reactions like (3)–(7) which makes it impossible to check whether the cross sections concerned are high enough to explain our observations. Snijkers¹⁸ gives values of 10⁻²¹–10⁻¹⁸ m² depending on whether the ion and neutral in the charge exchange collision are of the same species or not. It is therefore difficult to find out which ion–molecule reactions actually could be the cause of radical production in the sheath. Nevertheless, there are still many indications that inelastic collisions are the dominant mechanism of energy dissipation for ions in the sheath. Recent measurements have shown that the translational temperatures of all species in the plasma are constant over the volume and are close to room temperature for all

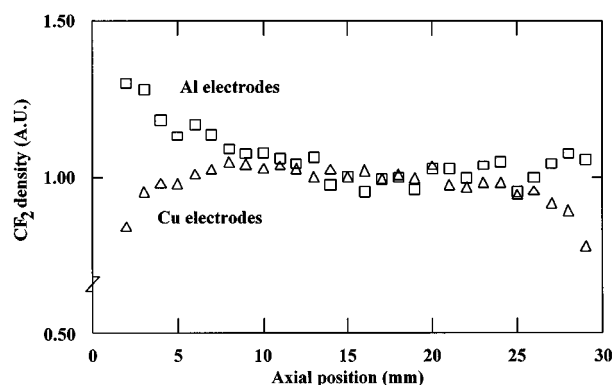


FIG. 5. Axial profile of the CF₂ density in a 300 mTorr CF₄ plasma and 100 W rf power in aluminum and copper electrodes. The characteristic increase of the CF₂ density is not observed when copper electrodes are used.

plasma conditions.¹⁵ Baggerman *et al.*¹⁹ have shown that most of the rf power in capacitively coupled rf plasmas is dissipated by ions in the sheaths, while the measurements of Snijkers suggest that the energy of the ions reaching the electrodes is much lower than the plasma potential. If the ionic energies were to be dissipated by elastic collisions, this would result in considerable heating of the gas, which is not observed in these plasmas. Therefore it is likely that most of this power is put into the dissociation of radicals.

Note that the CF₂ radical flux from the surface, given by Eq. (1) $\Phi_{\text{rad}} = 3 \times 10^{20} \text{ m}^{-2} \text{ s}^{-1}$ corresponds to a volume production rate of $2\Phi_{\text{rad}}A_{\text{el}}/V_{\text{pl}} = 5 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$, where A_{el} and V_{pl} denote the electrode surface and the plasma volume, respectively. This is comparable to the volume production of CF₂ by electron impact dissociation:¹³ $kn_e n_o = 5 \times 10^{-16} (10^{15}) (10^{22}) \text{ m}^{-3} \text{ s}^{-1} = 5 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$. This can explain the flatness of the axial profile in the glow region, indicating that in the glow there is an equilibrium between the gas phase production and gas phase loss. The latter may take place by three-body recombination with, e.g., F radicals.¹³

B. Dependence of profiles on the electrode material

In Fig. 4 the axial CF₂ profile is given for the case of a CF₄ plasma, but now using different electrode materials. In CF₄ plasmas the absolute densities of CF₂ are about six to eight times lower as compared with CHF₃ plasmas at the same conditions. Since in a CF₄ plasma no polymer-like layer is deposited on the electrodes (as happens in a CHF₃ plasma at this pressure), the electrodes stay clean^{20,21} and the electrode material may have an influence. In Fig. 5 it can be seen that the characteristic increase close to the electrodes does not happen with copper electrodes. Instead, a significant decrease is observed close to the electrodes. Moreover, the overall CF₂ densities are about 50% with copper electrodes as compared to Al electrodes. These results agree very well with the findings of Hansen *et al.*³

It is clear that the presence of copper electrodes induces a decrease of the CF₂ density near the electrodes, whereas the density profile in presence of aluminum electrodes is comparable to the profiles found in a CHF₃ plasma. This indicates

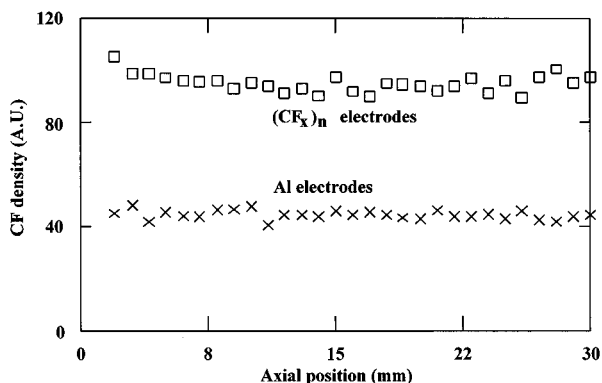


FIG. 6. Axial profiles of CF in a CHF_3 plasma at 50 mTorr, one with clean electrodes and one after depositing a thick $(CF_x)_n$ layer on the electrodes using a high pressure CHF_3 plasma. The rf power is 100 W in both cases.

that copper electrodes are a large sink of CF_2 radicals. Most likely radicals are also destroyed at the aluminum electrodes, but the reaction probability must be lower. This can be evidenced by comparing the absolute radical densities in a plasma using clean aluminum electrodes and electrodes covered with $(CF_x)_n$. Figure 6 shows the CF density profiles in a CHF_3 plasma at 50 mTorr for both cases. For this low pressure the profiles are flat, which can be attributed to enhanced diffusion and reduced gas phase losses. It can be seen that the absolute CF density in the presence of a clean electrode is only about half the density as that obtained with covered electrodes. From these data we can conclude that there is always a surface loss of radicals, the reaction probability being dependent on the wall material. This indicates that diffusion loss to the electrodes can play a major role in the loss processes of CF_2 radicals. This is not necessarily in contradiction with the fact that an increase is observed in the CF_2 density near the aluminum rf electrode. The production of CF_2 takes place in the sheath region, as described in Sec. IV A and a decrease of the CF_2 density very close to the electrodes can be observed. Such a decrease (~ 1.5 mm above the electrode) has indeed been reported by Booth *et al.*¹ A similar decrease very close to the electrode can also happen in a CHF_3 plasma, where a polymer-like layer is deposited on the electrodes. However, the sticking probability of CF_2 on such a layer is low,²² so surface losses are expected to be less important than in a CF_4 plasma.

C. Densities of CF_x radicals in pulsed fluorocarbon plasmas

In Figs. 7 and 8 measurements are shown of the CF_2 density in pulsed CHF_3 and CF_4 plasmas. It can be seen in Fig. 7 that the buildup of CF_2 density during the initiation phase of a CHF_3 plasma takes place on a much faster time scale than the decay in the afterglow. If CF_2 is produced by electrons or other charged species, the production should be more or less instantaneous, since the densities of charged species stabilize within a few tens of microseconds.¹³ Therefore the buildup time constant is in fact the time constant for CF_2 loss in the plasma. Both the buildup and decay rates of

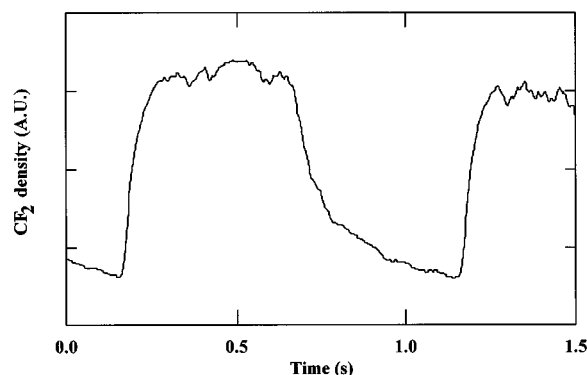


FIG. 7. Measurement of the relative density of CF_2 as a function of time in a modulated CHF_3 plasma at 300 mTorr gas pressure and 100 W rf power. It can be seen that the buildup of the CF_2 density during plasma initiation is much faster than the loss in the afterglow of the plasma. This suggests that during plasma operation gas phase loss of CF_2 plays an important role.

CF_2 are about one order of magnitude faster in CF_4 as compared to CHF_3 . In a CF_4 plasma the time scales for the buildup and decay of the CF_2 density are comparable. To get an idea of the buildup and decay rates the data have been fit using a first-order exponential. The results are given in Figs. 9 and 10. It can be seen in these figures that in a CF_4 plasma the time constants increase as a function of pressure, whereas in CHF_3 plasmas the time constants appear to be more or less constant with pressure.

The fact that the buildup of CF_2 after the ignition of a CHF_3 plasma is much faster than the loss in the afterglow suggests that during plasma operation the loss rate of CF_2 is significantly higher than in the afterglow. This confirms the conclusion, following from the hollow radical density profiles (Fig. 4), that gas phase loss processes are responsible for a large part of the total loss of CF_2 . Moreover, in a CHF_3 plasma the fact that the decay and buildup time constants decrease slowly as a function of pressure (Fig. 9) again indicates that diffusion loss to the electrodes probably does not play an important role. Since in a CHF_3 plasma at higher

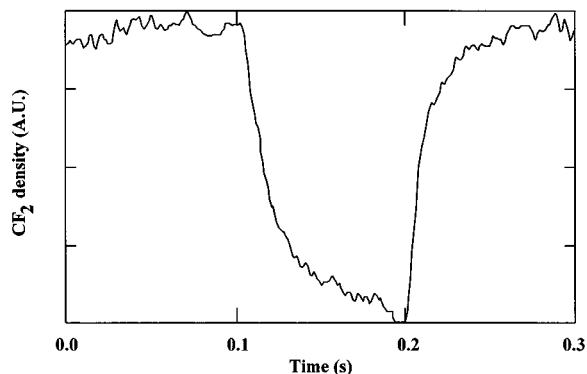


FIG. 8. Measurement of the relative density as a function of time in a modulated CF_4 plasma at 300 mTorr gas pressure and 100 W rf power. Both buildup and decay are much faster in CF_4 as compared to CHF_3 plasmas. Moreover, the buildup time constant is in the same order as the decay time constant.

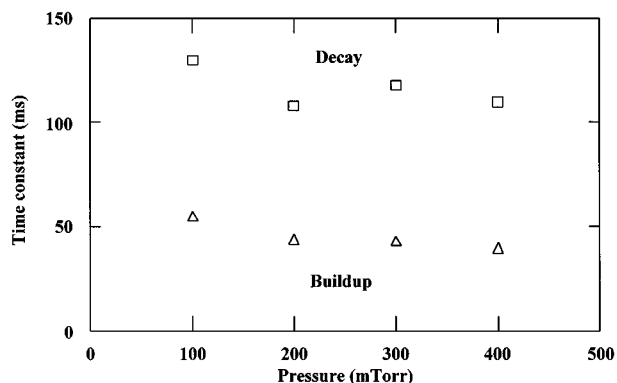


FIG. 9. The buildup and decay rates of CF_2 in a CHF_3 plasma as a function of the gas pressure. Both buildup and decay appear to be faster at higher pressures in CHF_3 .

pressures the electrodes are covered with $(CF_x)_n$ material, this confirms that the sticking probability of CF_2 on these surfaces is low. This has been established by Gray *et al.*²² who found the self-sticking coefficient of CF_2 to be 10^{-3} – 10^{-4} .

In a CF_4 plasma the buildup and loss rate are comparable (Fig. 10). This suggests that in CF_4 plasmas the loss rate of CF_2 in the plasma is probably not much higher than in the afterglow. Furthermore, in CF_4 plasmas the time constants increase more or less linearly as a function of the gas pressure. This confirms the conclusion in Sec. IV B, that, in presence of clean electrodes, diffusion loss of CF_2 to the electrodes is an important contribution to the total loss rate.

The same conclusion for CF follows from a study of its time constants. The decay time constant for CF radicals in a 100 mTorr CHF_3 with $(CF_x)_n$ covered electrodes, was found to be about three times larger than the decay time constant for CF_2 at the same conditions. This is in contrast to the behavior observed in CF_4 plasmas at 50 mTorr with clean electrodes by Booth *et al.*,¹ who found that the CF decay time constant is about five times lower than the one for CF_2 . It has been established that the decay rate increases by almost a factor of 2 if the electrode is cleaned thoroughly

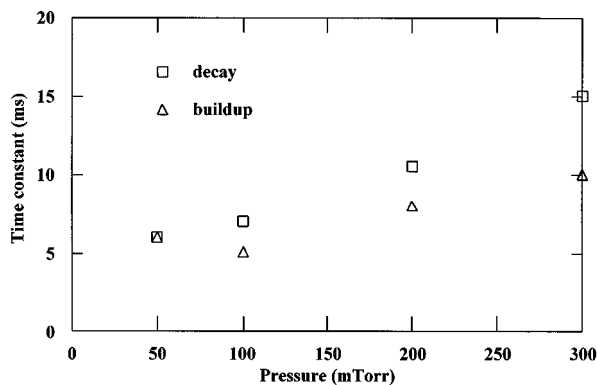


FIG. 10. The buildup and decay rates of CF_2 in a CF_4 plasma as a function of the gas pressure. In contrast to the behavior in CHF_3 , the buildup and decay appear to slow down at higher pressure.

(using a CF_4 plasma) before a low pressure CHF_3 plasma is started. With a clean electrode the CF density is lower, as shown in Fig. 5. The buildup rate for CF was found to be equal to the value found for CF_2 and it is six to eight times faster than the CF loss rate. However, this rate is still almost an order of magnitude slower than the decay rate found by Booth *et al.*¹ This is most likely due to a lower sticking coefficient of CF on $(CF_x)_n$ -covered surfaces as compared to on clean aluminum surfaces, as was observed for CF_2 .

V. CONCLUSIONS

Infrared absorption measurements using a tunable diode laser spectrometer were performed to yield space and time resolved densities of CF, CF_2 , and CF_3 in rf plasmas of CF_4 and CHF_3 at 13.56 MHz. Axial density profiles indicate that radicals are produced in the sheath region. Since all CF_x radicals show enhanced densities in the sheath, chemical sputtering is ruled out as a possible production mechanism for radicals at the surface. It is proposed that ion–molecule reactions in the sheath produce these radicals. There is very little surface loss of the CF and CF_2 radicals if the electrodes are covered by a $(CF_x)_n$ layer, e.g., in a high pressure (~ 300 mTorr) CHF_3 discharge. In the presence of clean metallic electrodes, e.g., in a CF_4 plasma, there is significant surface loss of radicals. For aluminum electrodes this results in a reduced radical density and a shorter decay time in the plasma afterglow. For copper electrodes surface loss becomes dominant, which results in a depletion of the radical densities near the electrodes.

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